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16. ABSTRACT

The theory of ion chromatography as a technique for analyzing ionic substances is discussed. The application of ion chromatography for analyzing ambient air samples is specifically described, with emphasis on determining sulfate, nitrate, and ammonium ions in aerosols and sulfur dioxide in the atmosphere.

17. KEY WORDS AND DOCUMENT ANALYSIS

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* Sulfates		07B
* Inorganic nitrates		07C
* Ammonium compounds		
* Sulfur dioxide		
* Chromatographic analysis		

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Ion chromatography

Accurate for the analysis of ions in solution, this newer form of analysis enables the analyst to directly assay many compounds that in the past were extremely difficult or impossible to analyze

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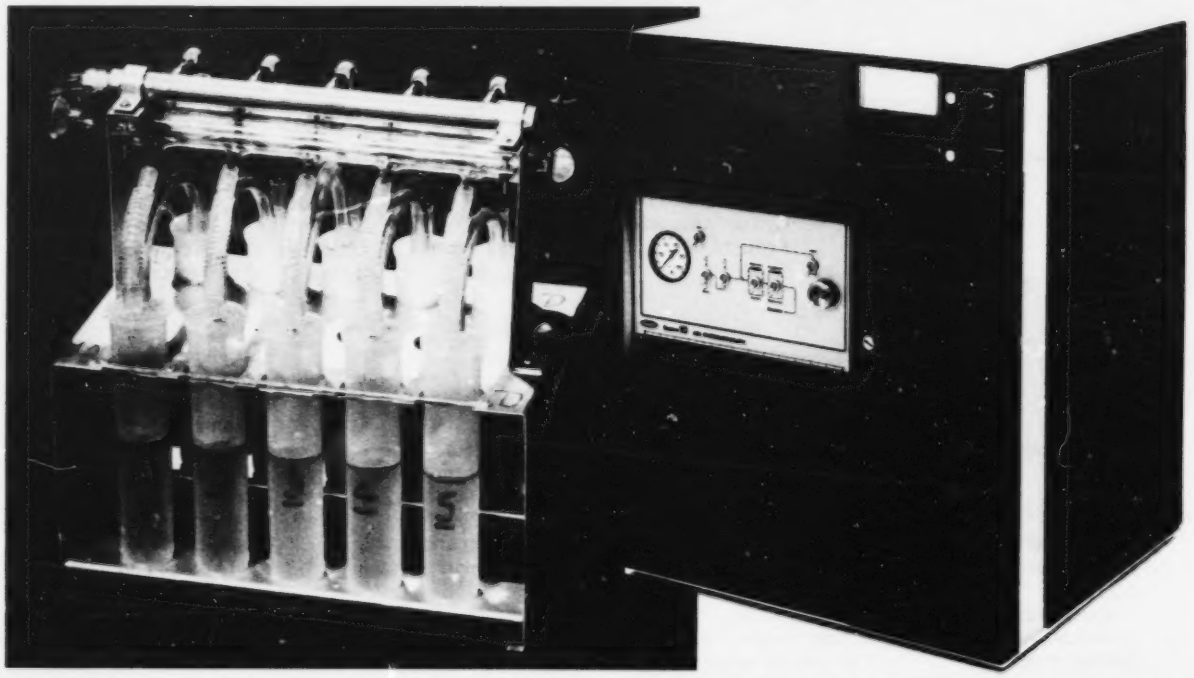
Introduced in 1975, Ion Chromatography (IC) is a relatively new technique for the analysis of various anions and cations, and is a significant addition to the ever-expanding field of chromatographic analysis. The originators, Hamish Small and co-workers of Dow Chemical, received the 1977 Applied Analytical Chemistry Award for its development.

Since its introduction, IC has seen phenomenal growth in most areas of analytical chemistry and has become a versatile and powerful technique for the analysis of a vast number of ions present in the environment or in biological tissues and fluids. Table 1 illustrates the wide variety of mixtures that have been analyzed with IC. This list suggests the potential of IC for analysis of numerous other environmental and biological samples. Table 2 lists many inorganic and organic chemicals that can be analyzed with IC.

The U.S. Environmental Protection Agency (EPA) became interested in ion chromatography in early 1976 because of the many different techniques used to assay various ionic pollutants. For example, there are over 200 available methods to assay for



Sampler & instrument. *Train collects ambient SO_2 which is converted to sulfate ion and routinely measured by the commercial instrument*

TABLE 1

Mixtures analyzed by ion chromatography

Aircraft exhaust emissions
Atmospheric aerosols
Atmospheric gases
Auto exhaust emissions
Boiler condensates
Boiler feed condensates
Brine solutions
Caustic solutions
Cerebrospinal fluid
Coal combustion products
Coal-fired utility boiler emissions
Coal gasification by-products
Coal liquefaction by-products
Combustion products
Commercial amines
Cosmetics
Cutting fluids
Diesel exhaust emissions
Drug additives
Electronic device process water
Engine coolants
Fertilizers
Flue gas desulfurization effluents
Food additives
Foods
Fuel cell effluents
Fuels
Geothermal waters
Groundwaters
High altitude air samples
High purity water
Human serum
Industrial atmospheres
Kraft black liquors
Marine cores
Milk
Nuclear fuel reprocessing streams
Ocean water
Oil shale water effluents
Paper mill effluents
Petrochemical effluents
Plating baths
Polymer combustion products
Pond water
Rainwater
Scrubber liquors
Smelter aerosols
Soil extracts
Spent sulfuric acid
Stack gases
Steam generator condensates
Surfactants
Turbine condensates
Uranium refining liquid
Urine
Waste effluents

sulfate and nitrate; most suffer from a lack of sensitivity or selectivity or are difficult and cumbersome to use.

Many employ chemical reagents of various types; some of these reagents are hazardous to human health. Ion chromatography offers EPA a single method with the capability to analyze not only sulfate and nitrate but numerous other pollutants as well. Figure 1 (IC analysis of F^-, Cl^-, NO_2^-, $PO_4^=$, Br^-, NO_3^-, and $SO_4^=$) and Figure 2 (IC analysis of Na^+, NH_4^+, and K^+) provide evidence of this.

Ion chromatography is a combination of the successful methodologies of ion exchange, liquid chromatography and conductimetric detection made feasible with the addition of eluant suppression. The process of ion exchange was known to provide excellent separation of ions by 1850; chromatographic separation of ions by ion exchange evolved in the early 1940's when ion-exchange resins became commercially available.

This is a powerful method for separation of inorganic and some organic ions through their relative affinities for an ion-exchange resin and enables the separation of many ionic species from a large variety of complex mixtures. Primarily because of the lack of a universal detector, however, ion exchange has never reached its full potential as an analytical tool.

Three of the most common detection methods that have been attempted with ion-exchange chromatography

TABLE 2

Chemicals analyzed by ion chromatography

Inorganic ions

Ammonia
Ammonia salts
Arsenate
Azide
Barium
Borate
Bromate
Bromide
Calcium
Carbonate
Cesium
Chlorate
Chloride
Chromate
Cyanide
Disulfide
Dithionate
Fluoride
Hydrobromic acid
Hydrochloric acid
Hypochlorite
Iodate
Iodide
Lithium
Magnesium
Nitrate
Nitrite
Orthophosphate
Potassium
Rhenate
Rubidium
Selenate
Silicate
Sodium
Strontium
Sulfate
Sulfide
Sulfite
Sulfur dioxide
Sulfuric acid
Tetrafluoroborate
Thiocyanate
Thiosulfate

Organic ions

Acetate
Adipate
Acrylate
Analine
Aromatic amines
Ascorbate
Benzoate
Butyrate
Butyl phosphate
Butylphosphonic acid
Citrate
Chloroacetate
Cyclohexylamine
Dibutyl phosphate
Dichloroacetate
Diethanolamine
Diisopropanolamine
Dimethylamine
Ethylmethylphosphonic acid
Formaldehyde
Formate
Formic acid
Fumarate
Gluconate
Glycolate
Hydroxycitrate
Hippuric acid
Isopropylmethylphosphonic acid
Itaconate
Lactate
Maleate
Malonate
Methacrylate
Methyl phosphonate
Monoethylamine
Monomethylamine
Monisopropanolamine
N-butylamine
Oxalate
Propionate
Phthalate
Pyruvate
Sarcosine
Succinic acid
Tartaric acid
Tetraethyl ammonium bromide
Tetramethyl ammonium bromide
Trichloroacetate
Triethanolamine
Triethylamine
Trifluoromethane sulfonate
Triisopropanolamine
Trimethylamine
Tri-n-butylamine

are photometry, refractive index, and conductivity. Photometric analysis is limited to ions which absorb light either individually or as a complex with another compound. The most common disadvantage of photometric methods, however, is that not all ionic species absorb light to a measurable amount or can be changed into or made to complex with molecules that do.

Refractive index methods are either not quite sensitive enough or do not show a sufficiently large difference between the refractive index of the sample ions and eluant ions to be useful in analysis.

Conductivity detection is the most widely preferred method because conductivity is a simple function of concentration and can be considered nearly linear at low concentrations. Because of the method's sensitivity and universal response to ionic species, conductivity detection with ion exchange was often attempted. These attempts met with limited success, however, because of the large background conductance produced by the eluant used to elute ions of interest from the chromatographic column. Successful combination of ion-exchange separation and conductivity detection required a method to remove background ions.

Introduction of the unique technique of eluant suppression in 1975 enabled the coupling of conductivity detection with the powerful resolution of ion-exchange chromatography. "Eluant suppression" is the removal or suppression of unwanted eluant ions from the eluant stream by means of a second ion-exchange column ("suppressor column") downstream from the analytical column. The resins in the second column suppress the conductivity of the eluant while leaving the ions of the sample unaffected for entry into the conductivity cell.

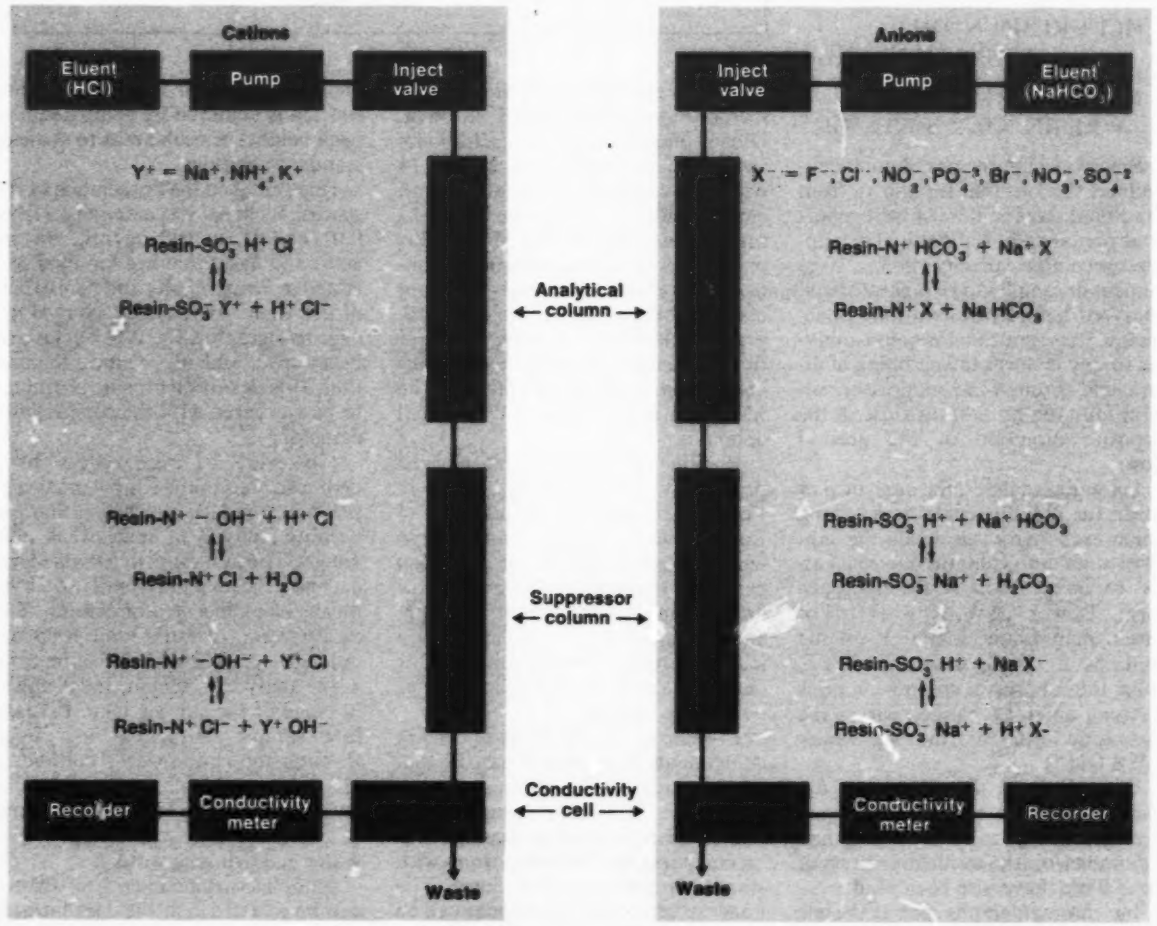
How it works

The principles of both anion and cation analysis are shown schematically. In each case, the instrumentation involves a sample inject valve, a pumping system for both eluant and suppressor column regeneration, an ion-exchange separator column, and a conductivity detector.

To better illustrate the suppression of background ions in the eluant consider the ion chromatographic analysis of the anions sulfate and nitrate in an aqueous eluant of sodium bicarbonate. If there were no suppressor column, the conductance of the sodium bicarbonate would be so high that it would mask the smaller concentration of individual nitrate and sulfate ions during entry into the conductivity cell.

The suppressor column is packed with a cation exchange resin of hydrogen. As the aqueous sodium bicarbonate solution passes through the suppressor column, the sodium ions of the eluant are exchanged with H^+ ions of the suppressor resin converting the bicarbonate ions to carbonic acid. Carbonic acid is a very weak acid with a much lower conductivity than the original aqueous sodium bicarbonate

Ion chromatographic principle



eluant—hence the term, "eluant suppression."

Following separation in the analytical column, sulfate and nitrate are also converted to their respective acids. The ions of sulfate and nitrate enter the conductivity detector as sulfuric acid and nitric acid in a weak solution of carbonic acid, making it possible to assay for these ions. Before the advent of eluant suppression, these types of assays would have been difficult to accomplish.

The suppressor column reactions for sulfate and nitrate anions with an aqueous bicarbonate eluant are as follows:

- $Na^+HCO_3^- + RESIN\text{-}SO_3^-H^+ = RESIN\text{-}SO_3^-NA^+ + H_2CO_3$
- $Na_2SO_4 + 2\,RESIN\text{-}SO_3^-H^+ = 2\,RESIN\text{-}SO_3^-Na^+ + H_2SO_4$
- $NaNO_3 + RESIN\text{-}SO_3^-H^+ = RESIN\text{-}SO_3^-Na^+ + HNO_3$

For cations, consider the analysis of NH_4^+ in an aqueous eluant of HCl. In this case, HCl is converted to H_2O and NH_4^+ is converted to its strongly conductive basic form (NH_4OH) that now enters the detector in a background of H_2O rather than HCl, as shown in the following equations:

- $HCl + RESIN\text{-}N^+OH^- = RESIN\text{-}N^+Cl^- + H_2O$
- $NH_4^+Cl^- + RESIN\text{-}N^+OH^- = RESIN\text{-}N^+Cl^- + NH_4^+OH^-$

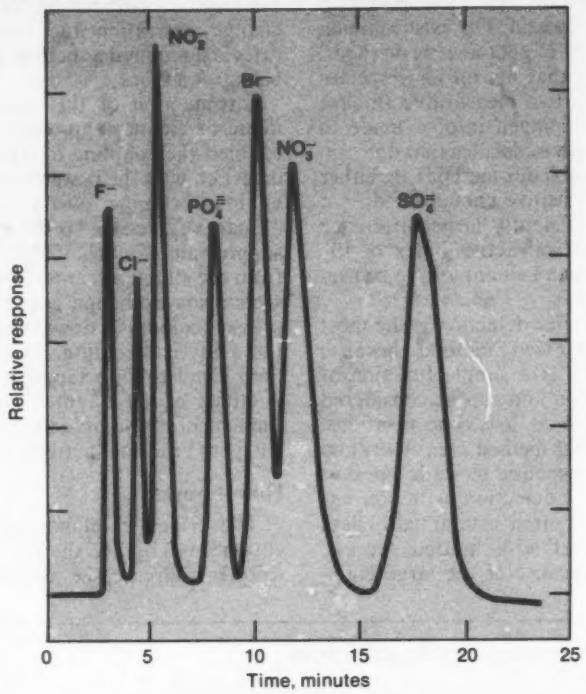
Since the suppressor column accumulates the ions that it removes from the eluant stream, it must be regenerated periodically for reuse. The suppressor column capacity allows a large number of samples to be separated and analyzed before regeneration is necessary. Regeneration for anion analyses simply involves the pumping of dilute acid through the suppressor column followed by a water rinse in the opposite direction of the normal flow.

For anion analyses, the analytical or separator column contains a strong anion exchange resin, while the suppressor column contains a strong cation exchange resin in the hydrogen form, Dowex 50W X 8 H^+. For cation analyses, the analytical column contains a strong cation exchange resin; the suppressor column contains a strong anion exchange resin in the hydroxide form (for example, Dowex 1 X 8 OH^-).

Depending on the separation desired, column dimensions range from 3 mm × 100 mm to 3 mm × 1000 mm. Columns with the inside diameters of up to 9 mm have also been used.

Ion chromatographs such as the one shown in the photograph are commercially available from the Dionex Corporation in Sunnyvale, California. Dionex manufactures three additional ion chromatographs: the Model 14 with the capability to analyze both cations and anions, and the Model 12 for on-line analysis. The Model 12 is particularly advantageous in the control of certain plant processes and plant effluents because it is completely programmable for full automatic operation of sample injection, column regeneration, and data handling. The Model 16 is the Model 14 with dual detectors.

FIGURE 1
Ion chromatogram of anions (negative ions)



Baseline resolution can be achieved practically for all anions shown in Figure 1 by judicious adjustment of flow, eluant strength, and column length. For example, better resolution can be obtained by lowering flow and/or eluant strength; in so doing, analysis time will increase, however. In many analyses, a low concentration of one ion can be measured in preponderance of another.

In some cases, the assay of certain components in a mixture may be sacrificed to achieve the required speed or resolution of other components. Species identification is accomplished by comparison of retention times with standards and since the detector is nondestructive the component can be collected for further identification by another analytical technique. Quantitation is achieved by comparison of peak heights or peak areas to those of standard solutions.

Depending on the dissociation of the species, IC linear response ranges from 0.01 μg/mL to 100 μg/mL. Strong acids and bases that are highly dissociated or ionized (pK_a and pK_b values of less than 7) are easily assayed ion chromatographically. Weak acids and bases (pK_a and pK_b values of more than 7) lack sufficient ionic character to be measured with the conductivity detector.

However, IC researchers have demonstrated that a simple modification of a standard ion chromatograph permits analysis of some weak acid anions. The minimum detectable level can now be extended still lower by means of a concentrator column. The concentrator column is 3 mm × 50 mm in length, packed with the same resin as the analytical column, and installed in place of the sample loop. Because large sample volumes can be pumped through the concentrator column, it allows the accumulation to detectable levels of extremely low concentrations of ions (for example, as found in rainwater and drinking water).

Samples varying from 1 to 100 mL can be injected into the concentrator column by hand or by syringe pump.

FIGURE 2

Ion chromatogram of cations (positive ions)

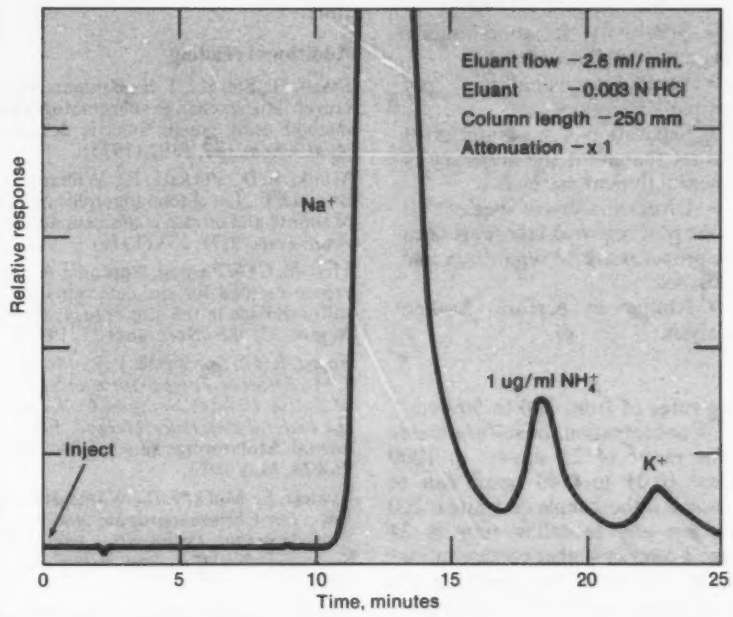
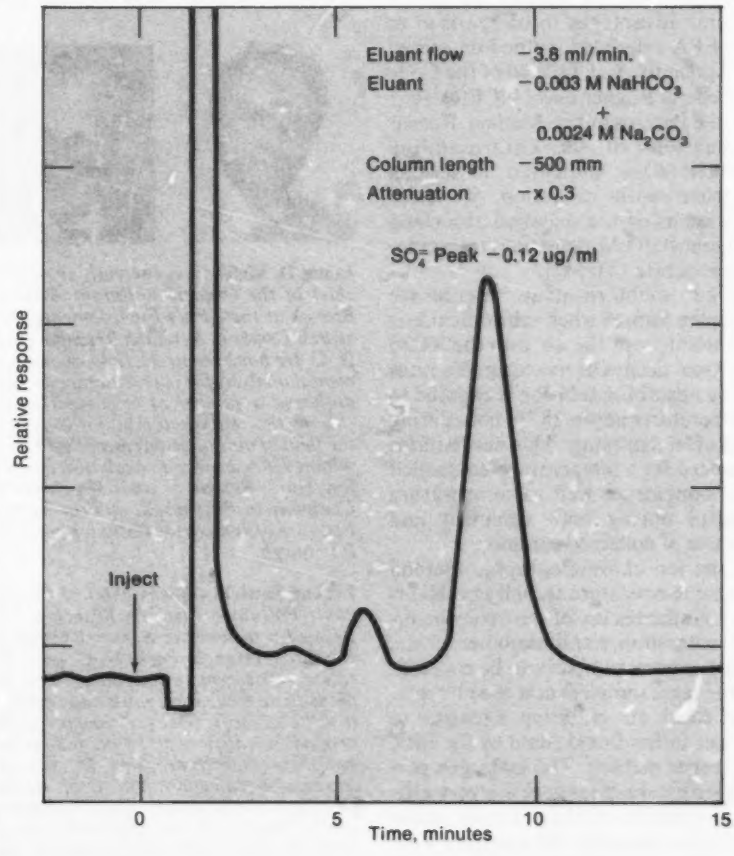


FIGURE 3

Ion chromatogram of SO_2 collected as sulfate



Samples also can be loaded into concentrator columns in the field and analyzed several days later without sample degradation.

Air pollutants

Most ionic pollutants currently assayed in ambient air are associated with particulates. In the Federal Register Reference Method for the Collection of Atmospheric Particulates, air is pulled through a glass fiber filter (8 in. × 10 in.) for 24 hours at approximately 1.7 m^3/min; at this flow rate, approximately 2400 m^3 of air are sampled per day with the Hi-Vol apparatus. There is more than enough sample collected on the Hi-Vol glass fiber filter to perform IC analysis for the various ions, even if they were present in concentrations as low as 1 $\mu g/m^3$.

Health effects researchers have become more concerned with the smaller suspended particulates capable of entering the respiratory system. The inhaled particulate (IP) range has been defined as 0–15 μm. As a result, much of the recent research effort has centered on a dichotomous sampler that collects IP in two fractions: <2.5 μm and 2.5–15 μm. A recent EPA-sponsored aerosol sampler comparison study showed that there is no ideal particulate sampler for all sampling and analytical requirements.

Since the dichotomous sampler collects small amounts of particulates (~1 mg/24 h; 1/100 of the Hi-Vol) and is a popular method for the collection of fine particles, it is important to note here that ion chromatograph has sufficient sensitivity to assay for sulfate and nitrate and other ions in the sample collected. Extensive research is ongoing both within EPA and the private sector to determine whether or not sufficient sample for the assay of some organic pollutants can be collected with the dichotomous sampler.

Other applications

Although emphasis in the past has been on the analysis of inorganic anions and cations, comparison of the data in Table 2 to the data published in the Proceedings of the First National Symposium on Ion Chromatograph Analysis of Environmental Pollutants held in April 1977 at RTP, N.C., indicates that methods for analysis of precursors of inorganic ions are being introduced.

Examples are ammonia, which can be converted to the ammonium cation, sulfur dioxide, which can be converted to the more stable sulfate anion, and nitrogen dioxide, which can be con-

verted to nitrite or nitrate ions. In addition, methods for the analysis of organic anions and cations are being introduced. These organic anions include the carboxylic acids (for example, acetate, adipate, maleate, oxalate, and tartarate) alkyl acids. Examples of organic cations are the alkyl and aryl amines.

As yet, very little work has been done with biological samples or with the precursors of ions. This is especially true of the organic ions. The aliphatic and aromatic amines have been studied to a slight extent. Thus far, aldehyde studies have consisted of the oxidation of formaldehyde and IC measurement of the resultant formic acid. There is much that can be done in the field of organic ions. Many organic and inorganic ions and their precursors have genotoxic properties that can affect even man (for example, the human genotoxicants b-naphthylamine, 4-aminobiphenyl, benzidine, chromate, arsenite, and possibly nitrate and nitrite). Since IC has simplified the analysis of the various types of compounds, its use should be expanded to the analyses of compounds that may be hazardous to human beings.

In addition to being a very powerful tool for the precise measurement of sulfate, nitrate, ammonium, and sodium ions in aerosols, IC can be used to measure precursors of anions and cations (for example, such gaseous pollutants as sulfur dioxide and ammonia). Methods for gaseous pollutants generally involve collection in an aqueous solution followed by conversion to ions that are suitable for analysis by IC.

Atmospheric SO_2 measurements

A method for collection and IC analysis of sulfur dioxide has been developed by EPA. The ion chromatographic method for SO_2 is currently under evaluation as a candidate equivalent method. Methods standardization testing will establish the best technical description to assure that users of the method will produce comparable high quality data. This method consists of the collection of ambient sulfur dioxide in a dilute solution of hydrogen peroxide that converts the sulfur dioxide to sulfate ion, which is then assayed by ion chromatography (Figure 3). Sulfur dioxide is absorbed from air in a solution of 0.6% hydrogen peroxide, using the gaseous pollutant sampling train.

Samples are collected at field locations and taken to a central laboratory for storage and eventual analysis by IC. This method is generally applicable to 24-hour measurements at sampling rates of from 200 to 500 cm^3/min. Concentrations of sulfur dioxide in the range of 25 $\mu g/m^3$ to 1000 $\mu g/m^3$ (0.01 to 0.40 ppm) can be measured if the sample flow rate is 200 cm^3/min and sampling time is 24 hours. Lower or higher concentrations can be measured by changing the sampling rate or time of sampling.

Reasons for the success of ion chromatography

- Sensitivity: detection limits at the parts-per-billion level
- Multi-ion analysis per sample
- Separation of most interfering species that limit the accuracy of other analytical methods
- Direct analysis of species that in the past required laborious sample preparation for separation and detection
- Ability to perform on-line analysis

Hydrogen peroxide collection and ion chromatographic analysis were developed as an improved alternate time-integrated method to measure sulfur dioxide in ambient air. Initial evaluation of the method indicated several advantages in comparison to the EPA reference method described in Appendix A of Title 40 of the Code of Federal Regulations (40CFR), Part 50: the Pararosaniline Method. Recent evaluations of the pararosaniline method have indicated a serious problem with collection of sulfur dioxide using the specified absorbing reagent [0.04 M potassium tetrachloromercurate (TCM)].

The dichlorosulfite mercurate complex formed when sulfur dioxide is absorbed from the air into the TCM solution, decays at unacceptable rates if the absorbing solution is exposed to temperatures above 25 °C both during and after sampling. This necessitates the need for a temperature-controlled gas sampler as well as temperature control during both shipment and storage of collected samples.

The ion chromatographic method has no temperature stability problems and eliminates use of the toxic chemical potassium tetrachloromercurate. Furthermore, samples can be collected in the same samplers now used by state and local air pollution agencies to collect sulfur dioxide data by the EPA reference method. The hydrogen peroxide absorbing reagent is a very efficient collector of sulfur dioxide; when a prefilter is used in the sampling train to remove aerosol sulfates, there are no apparent interferences. In addition, the sulfate formed in the sampling procedure is stable over a long period of time.

Additional reading

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James D. Mulik (l) *is currently the acting chief of the Organic Pollutant Analysis Branch at the EPA's Environmental Research Center in Research Triangle Park, N. C. He has been in the field of environmental analysis for over ten years and has authored a number of important publications that have had a major impact in the field of air pollution research. Prior to joining EPA, he was an analytical chemist for Gulf Research and Development Company in Pittsburgh, and the Mellon Institute of Industrial Research—also in Pittsburgh.*

Eugene Sawicki (r) *was chief of the Organic Pollutant Analysis Branch at the EPA's Environmental Research Center in Research Triangle Park, N. C. until his recent retirement in February 1979. He plans to do consulting work and continue to write scientific books. A member of the original scientific staff in the federal air pollution research program, Dr. Sawicki is a recognized expert in his field. He has served as a consultant on environmental carcinogenesis to the National Cancer Institute, and to various committees and advisory groups.*